

# Royal Society of Chemistry Theoretical Chemistry Group

## Newsletter – March 2005 25<sup>th</sup> Anniversary Graduate Student Meeting University of Nottingham April 13<sup>th</sup>, 2005

The annual meeting for presentations by final year graduate students in theoretical chemistry will be held on Wednesday 13<sup>th</sup> April in room C17 of the School of Chemistry, University of Nottingham, starting at 11 a.m. Travel details can be found at: <http://www.nottingham.ac.uk/chemistry/icavs/TRAVEL.pdf> and a map of the campus at: <http://www.nottingham.ac.uk/campuses/university-park/university-park-map.phtml>

This year marks the 25th anniversary of the first graduate student meeting organised by the Theoretical Chemistry Group. To celebrate this occasion, in addition to the talks by final year postgraduate students in theoretical/computational chemistry, we will be having a poster session for second year postgraduate students and there will be plenary lectures by three of the speakers from the first TCG graduate student meeting in 1980: Professor Patrick Fowler (Exeter); Professor Sally Price (UCL); and Professor Jonathan Tennyson (UCL).

### PROGRAMME

11:00	Prof. I. H. Williams	<i>Introduction</i>
11:00	Prof. Patrick W. Fowler (Exeter)	<i>Fullerenes and their exotic friends</i>
11:30	Andy May (Bristol)	<i>Density fitting in explicitly correlated electronic structure theory</i>
11:55	Thomas W. Keal (Durham)	<i>Semi-empirical fitting of exchange-correlation functionals</i>
12:20	LUNCH	(including poster session and tour of SUN high performance computing facility)
14:00	Prof. Sarah (Sally) L. Price (UCL)	<i>Organic crystal structure prediction: an application of computational chemistry that can make useful predictions?</i>
14:30	Mahesh Sundararajan (Manchester)	<i>Structure and function of the iron–sulfur protein Rubredoxin, studied by QM/MM methods</i>
14:55	Robert J. Barber (UCL)	<i>A new high accuracy water line list: computation and applications</i>
15:20	Susan Larkin (Imperial College)	<i>Excited states, conical intersections and the ONIOM method</i>
15:45	TEA	

(Continued overleaf)

- 16:15 Adam Kirrander (Oxford) *H<sub>2</sub>: a simple molecule with complex dynamics*
- 16:40 James Munro (UCL) *H<sub>3</sub><sup>+</sup> to dissociation and beyond*
- 17:05 Mohammad Noh Daud (Bristol) *Photodissociation of N<sub>2</sub>O*
- 17:30 Prof. Jonathan Tennyson (UCL) *Molecular physics and the mass of the neutrino*
- 18:00 Announcement of Coulson Prize 2005
- 18:15 CLOSE

We are grateful to Sun Microsystems Ltd. for generous support for this meeting.

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## Abstracts

### Plenary Lectures

**Patrick W. Fowler (Exeter)**

*Fullerenes and their exotic friends*

Fullerenes are n-atomic carbon polyhedra with 12 pentagonal and (n/2-10) hexagonal faces. Their electronic configurations and many of their properties are usefully predicted by purely graph-theoretical arguments. Fullerenes are essentially spherical, but why should Nature stop at the sphere? Fullerene-like graphs can be embedded as maps in four closed surfaces (sphere, torus, Klein bottle, projective plane), all with characteristic Huckel rules derived by topological double-cover arguments, and some with experimental realisations. An extended argument shows the general relationship between energy levels/orbitals of Moebius and cylindrical conjugated systems, with some surprising results.

**Sarah (Sally) L. Price (University College London)**

*Organic crystal structure prediction: an application of computational chemistry  
that can make useful predictions?*

When 25 years ago, I was researching the intermolecular forces between hydrogen molecules, it seemed unlikely that accurate intermolecular potentials would ever be developed for organic molecules. However, now model potentials, partially derived from the molecular charge density, form a major part of the input into searches for energetically feasible crystal structures. The practical importance of predicting organic crystal structures and polymorphism means that theoreticians working in this area have been challenged to predict crystal structures given only the chemical diagram. Whilst there have been some successes in these blind tests, and indeed some crystal structures have been predicted before they have been found experimentally, there is still a long way to go before we have a quantitative theory that can predict the crystallisation of organic molecules reliably.

## **Jonathan Tennyson (University College London)**

### *Molecular physics and the mass of the neutrino*

It is now established that neutrinos have a mass but only an upper limit for this mass is known. The best prospect for a laboratory determination of the mass of a neutrino appears to be tritium endpoint experiments. The KATRIN collaboration is preparing new, high sensitivity measurement based on precise measurements of tritium molecule decays. These measurements can only be interpreted using detailed information on the (molecular) products of the decay. Progress on calculations which (a) characterise the decay processes, (b) allow for errors in both the temperature and isotopic composition of the sources, and (c) consider the effects of other possible processes in the tritium source will be presented.

## **Postgraduate Lectures**

### **Robert J. Barber (University College London)**

#### *A new high accuracy water line list: computation and applications*

Water is the third most common molecule in the Universe. Its spectrum is particularly rich and H<sub>2</sub>O lines have been detected in locations as diverse as: the ISM, comets, Mira variables, sun spots, brown dwarfs and red giants. Nevertheless, only a very small fraction of the lines in the water spectrum are known experimentally, and if for no other reason than sheer number, it seems inevitable that astronomers will continue to use theoretical data when exploring the nature of these objects. All previous water line lists suffer from incompleteness and inaccuracy (particularly at higher energies). We have produced a new list, BT2, that addresses these shortcomings.

Our *ab initio* computation has employed the best available potential energy and dipole moment surfaces to perform quantum mechanical nuclear motion (rotation-vibration) calculations using the DVR3D suite of codes. The preliminary calculations which established the optimum parameters for the basis function and the ro-vibrational basis set were also fundamental in producing accurate line positions. The BT2 water line list contains in excess of 500 million transitions. It will be published shortly [1], but it is already finding laboratory [2] and astronomical applications [3,4].

[1] R. J. Barber, J. Tennyson *et al.* (in prep.).

[2] P.-F. Coheur *et al.* *J. Chem. Phys.* **122** (2005).

[3] N. Dello Russo *et al.* *ApJ* **621** (2005).

[4] D. P. K. Banerjee, R. J. Barber *et al.* (in prep.).

### **Thomas W. Keal (Durham)**

#### *Semi-empirical fitting of exchange-correlation functionals*

We describe our continuing work to improve the quality of semi-empirical exchange-correlation functionals in DFT by fitting to a diverse range of properties with a large number of training molecules. This highly empirical approach can result in significant improvements in accuracy over competing generalised gradient approximation (GGA) and hybrid functionals.

Previous studies [1,2] have shown that a simple gradient correction to the local density approximation can provide NMR shielding constants for challenging main-group nuclei that are 2-3 times more accurate than those of conventional GGAs and hybrids. These functionals were denoted KT1 and KT2. By adding one additional exchange term, the KT3 GGA functional was developed [3], which retained the quality of shielding constants while substantially improving the performance for other properties. In particular, it gives atomisation energies that are as accurate as the best competing GGA functionals and equilibrium molecular bond lengths that are as accurate as the best hybrid functionals.

However, its performance for classical reaction barriers is relatively weak. We describe our attempts to develop new GGA and hybrid functionals that give improved reaction barriers while retaining the high quality performance of KT3 for other properties.

[1] T.W. Keal and D. J. Tozer, *J. Chem. Phys.* 2003, **119**, 3015.

[2] M.J. Allen, T.W. Keal and D.J. Tozer, *Chem. Phys. Lett.* 2003, **380**, 70.

[3] T.W. Keal and D.J. Tozer, *J. Chem. Phys.* 2004, **121**, 5654.

### **Adam Kirrander (Oxford)**

#### *H<sub>2</sub>: a simple molecule with complex dynamics*

The hydrogen molecule may be the simplest of molecules, but its highly complex and non-adiabatic dynamics is far from simple. Due to the low mass of the nuclei, separation into electronic, vibrational and rotational energy becomes difficult for excited states and the energy levels are much better described as mixed rovibronic levels. Furthermore, highly excited rovibronic levels couple to the ionisation and dissociation continua. These states have a limited lifetime, which gives them an inherent line width in spectral measurements. We apply Multichannel Quantum Defect Theory (MQDT) and R-matrix theory to calculate and interpret preionised and predissociated hydrogen spectra. Furthermore, we show how to obtain branching ratios for the dissociative reactions. These branching ratios are highly relevant to astrophysical processes in diffuse interstellar clouds. Finally, we intend to emphasise how our theoretical treatment gives a physically intuitive understanding of the dynamics of highly excited molecules in general.

### **Susan Larkin (Imperial College London)**

#### *Excited states, conical intersections and the ONIOM method*

The use of *ab initio* methods to find conical intersections can be very time-consuming and if the molecule is too large, it is impossible. Using a hybrid method, ONIOM, we have been able to successfully locate conical intersections geometries in a fraction of the time of the *ab initio* method. As this presentation illustrates, one ONIOM method in particular was successful at reproducing accurate relative energies between the conical intersection geometry and the s1 minima.

### **Andy May (Bristol)**

#### *Density fitting in explicitly correlated electronic structure theory*

Accurate quantum chemical calculations are limited to small molecules partly owing to the poor convergence of orbital based methods. One solution to this problem is to use explicitly correlated electronic structure theories [1]. These methods give very accurate energies for small molecules, but become computationally difficult for larger systems. The problem arises from the need to compute three- and four-electron integrals, which are both complicated and extremely numerous. The R12 methods developed by Kutzelnigg and Klopper [2-4] use Resolution of Identity (RI) to approximate these integrals and have allowed calculations on chemically significant problems.

In this work we develop a version of MP2-R12 theory for an arbitrary correlation factor and derive recurrence relations for the integrals needed when the correlation factor is a frozen Gaussian geminal [5]. We show that the accuracy of MP2-R12 methods can be greatly improved by replacing the conventional  $r_{12}$  factor with a function of  $r_{12}$  better able to describe the shape of the correlation hole. It is shown that the errors associated with using linear  $r_{12}$  (rather than something better) are at least an order of magnitude greater than the errors associated with RI or other approximations in the MP2-R12 class of methods. The impact on our aim to do accurate quantum chemistry in reasonably compact orbital basis sets is assessed.

- [1] E. A. Hylleraas, *Z. Phys.* **54**, 347 (1929).  
 [2] W. Kutzelnigg, *Theor. Chim. Acta* **68**, 445 (1985).  
 [3] W. Klopper and W. Kutzelnigg, *Chem. Phys. Lett.* **134**, 17 (1987).  
 [4] W. Kutzelnigg and W. Klopper, *J. Chem. Phys.* **94**, 1985 (1991).  
 [5] A. J. May and F. R. Manby, *J. Chem. Phys.* **121**, 4479 (2004).

### James Munro (University College London)

#### *H<sub>3</sub><sup>+</sup> to dissociation and beyond*

In the 1980's Carrington et al [1] recorded a CO<sub>2</sub> laser predissociation spectrum of H<sub>3</sub><sup>+</sup>. The spectrum proved to be remarkable and quite unique. Over 20 years later and some progress has been made but the spectrum remains completely unassigned. Recently we have made progress in understanding the dissociative behaviour of H<sub>3</sub><sup>+</sup> by performing very large calculations on a supercomputer using the PDVR3D program [2]. These improve on previous calculations [3,4] in a number of ways. We have discovered a series of asymptotic vibrational states, states with very long range behaviour which could have important consequences for the spectroscopy of H<sub>3</sub><sup>+</sup>.

- [1] A. Carrington I.R. McNab, *Acc. Chem. Res.* **22** (1989) 218-222.  
 [2] H.Y. Mussa, J. Tennyson, *Comp. Phys. Comm.* **128** (2000) 434-445.  
 [3] M.A. Kostin, O.L. Polyansky, J. Tennyson, *J. Chem. Phys.* **118** (2003) 3538-2542.  
 [4] V.A. Mandelshtam, H.S. Taylor, *J. Chem. Soc. Fara. Trans.* **93** (1997) 847.

### Mohammad Noh Daud (Bristol)

#### *Photodissociation of N<sub>2</sub>O*

Adiabatic potential energy surfaces for the six lowest singlet electronic states of N<sub>2</sub>O (X<sup>1</sup>A', 2<sup>1</sup>A', 3<sup>1</sup>A', 1<sup>1</sup>A'', 2<sup>1</sup>A'' and 3<sup>1</sup>A'') have been computed using an *ab initio* multireference configuration interaction (MRCI) method and a large orbital basis set (aug-cc-pVQZ). The potential energy surfaces display several symmetry related and some non-symmetry related conical intersections. Total photodissociation cross sections and product rotational state distributions have been calculated for the first ultraviolet absorption band of the system using the adiabatic *ab initio* potential energy and transition dipole moment surfaces corresponding to the lowest three excited electronic states. In the Franck-Condon region the potential energy curves corresponding to these three states lie very close in energy and they all contribute to the absorption cross section in the first ultraviolet band. The total angular momentum is treated correctly in both the initial and final states. The total photodissociation spectra and product rotational distributions are determined for N<sub>2</sub>O initially in its ground vibrational state (0,0,0) and in the vibrationally excited (0,1,0) (bending) state. The resulting total absorption spectra are in good quantitative agreement with the experimental results over the region of the first ultraviolet absorption band, 160 nm to 220 nm. All of the lowest three electronically excited states [<sup>1</sup>Σ<sup>-</sup>(1<sup>1</sup>A''), <sup>1</sup>Δ(2<sup>1</sup>A') and <sup>1</sup>Δ(2<sup>1</sup>A'')] have zero transition dipole moments from the ground state [<sup>1</sup>Σ<sup>+</sup>(1<sup>1</sup>A')] in its equilibrium linear configuration. The absorption becomes allowed only through the bending motion of the molecule. The <sup>1</sup>Δ(2<sup>1</sup>A') ← X<sup>1</sup>Σ<sup>+</sup>(1<sup>1</sup>A') absorption dominates the absorption cross section with absorption to the other two electronic states contributing to the shape and diffuse structure of the band. It is suggested that absorption to the bound <sup>1</sup>Δ(2<sup>1</sup>A'') state makes an important contribution to the experimentally observed diffuse structure in the first ultraviolet absorption band. The predicted product rotational quantum state distribution at 203 nm agrees well with experimental observations.

## **Mahesh Sundararajan (Manchester)**

### *Structure and function of the iron–sulfur protein Rubredoxin, studied by QM/MM methods*

Iron–Sulfur proteins are an important class of electron transfer protein acting as electron sinks for many biological reactions. One such iron–sulfur protein is Rubredoxin (Rd) which has a high spin iron centre, tetrahedrally coordinated to four cysteine sulfurs. We have explored the redox chemistry of Rd using both density functional theory (DFT) and semi–empirical methods. These latter methods require quite modest computing resources, but their accuracy is often suspect, particularly when the molecule contains a transition metal atom. However, a possible way forward is to develop parameters for use in semi–empirical MO studies that are tailored for a particular chemical situation, the so–called specific reaction parameters SRP [1]. We first describe a possible strategy to extend this approach to transition metal complexes [2]. Based on fitting to DFT data for redox site analogue, a PM3 parameter set for iron has been developed, which is appropriate for the active site of iron sulfur proteins having a single iron atom, and further tested on similar molecules. The use of these parameters within a two layer ONIOM treatment of the protein Rd, yields accurate predictions of the effect of the protein on both Fe–S bond lengths and inner sphere reorganization energies [3]. We also describe calculations on similar proteins in which the central metal atom or the cysteine ligands are mutated.

[1] Rossi, I., and Truhlar, D.G. *Chem. Phys. Lett.* **1995**, 233, 231–236.

[2] Mohr, M., McNamara, J.P., Wang, H., Rajeev, S.A., Ge, J., Morgado, C.A., and Hillier, I.H. *Faraday Discuss.* **2003**, 124, 413–428.

[3] Sundararajan, M., McNamara, J.P., Hillier, I.H., Wang, H., and Burton, N.A. *Chem. Phys. Lett.* **2005**, 404, 9–12.

## **Report on Previous Meeting**

### *Theoretical Chemistry Days No. 12*

A full-day symposium *Controlling Atoms and Molecules: In Theory and Practice* (co-organised with the Chemical Physics Group of the Institute of Physics) was held on Wednesday 10<sup>th</sup> November 2004 at University College, London. Plenary lectures were given by Ferenc Krausz (Vienna) and Hershel Rabitz (Princeton), who were very well supported by a number of speakers from the UK: Stuart Althorpe (Nottingham), Gabriel Balint-Kurti (Bristol), Helen Fielding (University College London), Simon Hooker (Oxford) and Jeremy Hutson (Durham). The speakers gave an excellent overview of experimental and theoretical approaches to the control and manipulation of atoms and molecules. The meeting was well attended and the lectures stimulated lively discussion. The Theoretical Chemistry Group is grateful to the Chemical Physics Group of the Institute of Physics (especially June McCombie and Stephen Price for co-organizing the meeting) and to *Molecular Physics* and *Streamline Computing* for sponsorship.

The date and subject of *Theoretical Chemistry Days No. 13* will be announced shortly.

## **Forthcoming Meetings**

### ***Biomolecular Simulation Summer School***

University of Cardiff, Wales (16-19 July 2005).

This School (which is being organized by the Theoretical Chemistry group, in collaboration with CCP5) is intended for new PhD students and postdocs working in the area of biomolecular simulation and will provide a detailed introduction to the methodology, practical sessions on computational methods and examples of the power and versatility of simulation methods. The School will be limited to 20 participants and a preselection procedure will be applied. Applicants will be required to give details of qualifications and research experience. The cost will be £110, payable upon acceptance of a place, and includes accommodation and meals.

Further details and online application/registration are available by following the links from the Theoretical Chemistry Group web page: <http://www.tc.bham.ac.uk/~roy/TCG/TCG.html>.

We are grateful to the Royal Society of Chemistry for financial support through the Travel Grant scheme and to CCP5 and the Molecular Graphics and Modeling Society for additional support.

### ***2005 American Conference on Theoretical Chemistry***

University of California, Los Angeles, USA (16-21 July 2005).

Web site: <http://www.conferences.ucla.edu/actc/>

### ***CCP6 Workshop on Vector Correlation and Alignment in Chemistry***

Bristol, 24-27 July 2005

Web site: <http://www.chm.bris.ac.uk/ccp6-workshop>

Registration deadline 31st March

Joint Organisers:     Gabriel Balint-Kurti (Gabriel.Balint-Kurti@Bristol.ac.uk)  
                          Marcelo Miranda (M.Miranda@chemistry.leeds.ac.uk)

### ***11<sup>th</sup> International Conference on the Applications of DFT in Chemistry and Physics***

Geneva, Switzerland (11-15 September 2005).

Web site: <http://dft2005.unige.ch/>

## Vacancies

### Postdoctoral Position, University of Bristol

EPSRC-funded PDRA position to work with Dr F R Manby, Dr J N Harvey and Dr A J Mulholland (Centre for Computational Chemistry, School of Chemistry, University of Bristol) on the development of accurate QM/MM methods for modelling enzyme catalysis. Please see the Bristol vacancies web site for details: <http://www.bris.ac.uk/boris/jobs>

### Postdoctoral Position, University College London

An EPSRC-funded postdoctoral position is available for a computational chemist to work under the supervision of Dr Nik Kaltsoyannis at University College London on the electronic structure of molecular complexes of the actinide elements. The two main topics to be addressed are (i) metal-metal bonding and (ii) the role of multi-configurational wavefunctions in the actinocenes. Experience with one or more of the following codes is desirable: ADF, Gaussian, Molpro, Molcas.

Applicants should have at least submitted their PhD thesis prior to taking up the appointment. The post is available from 1<sup>st</sup> July 2005 for one year in the first instance (renewable) at a salary on the RAIA scale (currently £19,460 to £29,128). The starting salary will be no higher than point 6 on the scale (£21,640), and will be supplemented by the UCL London Allowance of £2,330.

Further details are available at <http://www.chem.ucl.ac.uk/people/jobs.html> or from Dr Nik Kaltsoyannis:

Department of Chemistry,  
University College London,  
20 Gordon Street,  
London WC1H 0AJ  
Email: [n.kaltsoyannis@ucl.ac.uk](mailto:n.kaltsoyannis@ucl.ac.uk)

Applications should be sent to Dr Nik Kaltsoyannis (contact details above) with a full curriculum vitae, including research experience, scientific publication list and the names and contact details of at least two referees, and with the following two forms completed

[www.ucl.ac.uk/hr/docs/download\\_forms/recruitment\\_selection\\_I.doc](http://www.ucl.ac.uk/hr/docs/download_forms/recruitment_selection_I.doc)

[www.ucl.ac.uk/hr/docs/download\\_forms/recruitment\\_eo.doc](http://www.ucl.ac.uk/hr/docs/download_forms/recruitment_eo.doc)

UCL Taking Action for Equality.

The closing date for applications is Monday 9<sup>th</sup> May 2005.

### PhD Studentship, University College London

**Development of accurate intermolecular potentials for organic molecules, and their application to the solid state.**

This recently funded EPSRC project includes a studentship for theoretical and computational work to be done under the supervision of Prof S L Price, in collaboration with Dr M Leslie, Dr AJ Stone and Dr AJ Misquitta. Further details on <http://www.chem.ucl.ac.uk/research/postgraduate/documents/pricesl05.html> and from [l.s.price@ucl.ac.uk](mailto:l.s.price@ucl.ac.uk).

## **Group Matters**

### **Committee**

The TCG Committee currently consists of Professor Ian Williams (Chair – Bath), Dr Roy Johnston (Secretary & Treasurer – Birmingham), Dr Stuart Althorpe (Nottingham), Dr Mike Bearpark (Imperial College, London), Professor Jonathan Hirst (Nottingham), Dr Nik Kaltsoyannis (University College, London), Dr Fred Manby (Bristol), Dr David Tozer (Durham), Dr John Wilkie (Birmingham) and Dr Tim Wright (Nottingham).

### **New Group Secretary/Treasurer**

Roy Johnston's term of office is due to finish at the end of 2005. The new Secretary and Treasurer of the Group (who has been elected by the TCG Committee) is Professor Jonathan Hirst (Nottingham), who will serve for a period of 4 years, from January 2006.

### **Web Manager**

John Wilkie (Birmingham) has been appointed web manager for the Group. The Group web page (maintained by the RSC) is at <http://www.rsc.org/tcg>. More details about the Group, forthcoming meetings, etc. can also be found at <http://www.tc.bham.ac.uk/~roy/TCG/TCG.html>.

### **Committee Vacancy**

There will be a vacancy for one person to serve on the TCG Committee for a period of 3 years, from January 2006. If you would like to volunteer or to nominate someone for this position (please check with the potential nominee first) please contact the Secretary ([r.l.johnston@bham.ac.uk](mailto:r.l.johnston@bham.ac.uk)) by **30 April**.

### **Membership**

RSC members can join the Theoretical Chemistry Group by ticking the appropriate box on the RSC subscription form and paying the annual fee of £4. If you are an RSC member and wish to join part way through the year or if you are not a member of the RSC, please contact the RSC Membership Department. (For details see <http://www.rsc.org/members/memindex.htm>). Please encourage your colleagues, postdocs and postgraduate students to join the Group.

If you are a member of the Group but are not on the e-mailing list, or if your e-mail address has recently changed (a number of e-mail addresses regularly fail), please contact the Secretary.

### **Newsletters**

Please send material for inclusion in future newsletters (and for e-mail circulation and advertisement on the Group web site) to the Secretary, Dr R. L. Johnston, School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT (e-mail: [r.l.johnston@bham.ac.uk](mailto:r.l.johnston@bham.ac.uk)).

### **TCG Annual Report 2004**

The annual report of the Group for 2004 will shortly be posted on the Group web page at: <http://www.rsc.org/tcg>.